EFFECT OF SIZE ON THE ELECTRICAL RESISTANCE OF THALLIUM AT HELIUM TEMPERATURES

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The temperature dependence of and the effect of size on the electrical resistance of polycrystalline cylindrical thallium samples of ≥99.999% purity and having a residual resistance $\rho_0/\rho_{293} = 2.3 \times 10^{-5}$ were investigated in the temperature range 5–2°K. It was found that in this temperature range, the resistance of a bulk thallium sample varied as $T^{4.6}$. For thinner samples, the power exponent of T was smaller: for the thinnest wire studied (0.125 mm), it was 4.2. A mean free path $\lambda_0 = 1$ mm governed by impurities and $\rho\lambda = 4.3 \times 10^{-11} \Omega \cdot cm^2$ were estimated at T = 0°K from the size effect by assuming diffuse scattering of electrons from the walls. From $\rho\lambda$, the number of electrons per atom could be calculated: it was found to be 0.15.

THE nature of electrical conduction at low temperatures depends heavily on the purity of the investigated metal. When very pure metals become available, new properties of the electrical conductivity were discovered [1] and the theoretical dependence predicted earlier by Bloch [2] was confirmed experimentally. Up to now, the resistance of about 25 very pure metals has been investigated in sufficient detail. Nevertheless, the electrical conductivity of many metals has either hardly been investigated or such investigations have been carried out on very impure samples. One such metal is thallium. There is a paper by de Haas et al.[3] which describes an investigation of the electrical conductivity of fairly impure thallium in the temperature range from 20 to 2.5°K. From the temperature dependence of the lattice resistivity $\rho(T)$, given in that paper in logarithmic coordinates, it follows that $\rho(T) \propto T^4$ in the temperature range 3.5–8°K. At other temperatures, the power exponent m of T has been found to be less than 4. Zavaritskiĭ [4] has mentioned, without giving any experimental details, that for very pure thallium $\rho(T) \propto T^5$. These two papers do not contain sufficient data to deduce the nature of the temperature dependence of the electrical resistance of pure thallium.

The present investigation was undertaken to determine this temperature dependence and the dependence on the size of a sample in the most interesting low-temperature region—at helium temperatures.[1)] Moreover, it also seemed interesting to determine the effect of size on the resistance of thallium, from which the electron mean free path λ, governed by the impurities present in the sample, could be estimated. Knowing the mean free path is important for its own sake and as an indication of the possibility of carrying out other low-temperature experiments on thallium of known purity.

PREPARATION OF THE SAMPLES AND THE APPARATUS

All measurements of the resistance were carried out on polycrystalline cylindrical wires of 2.5–0.125 mm diameter, prepared from thallium of Tl-00 grade and ≥ 99.99% purity.

Thick samples, 2.5–0.5 mm in diameter and 120–60 mm long, were prepared by filling, with liquid thallium (in the manner described earlier [5]), molybdenum glass capillaries of suitable size.[2)] Because of the large amounts of oxides and gases dissolved in thallium, which make it impossible to prepare a monolithic (free of blisters) cylindrical sample, a lump of the metal was heated for 5–10 min at 400–500°C in vacuum before being used to fill a capillary. During such heating, the thallium was well outgassed and the resultant cylindrical sample had practically no blisters due to the gases evolved from it. The glass capillaries were dissolved in hydrofluoric acid and the samples themselves were then etched in HNO_3 and washed in ethyl alcohol.

Thin samples (of < 0.5 mm diameter) were prepared by rolling wires. 0.5–0.4 mm in diameter and 20–50 mm long, between two glass plates with carefully cleaned surfaces; this was followed by etching in HNO_3 and washing in alcohol. The diameters of the samples were determined, with an accuracy of 0.01 mm, using a microscope. To estimate and eliminate a possible ellipticity of the samples, the diameter of a wire was determined at several points on its circumference and along its length. It was found that, as a rule, the ellipticity was small and within the limits of the accuracy attainable with a microscope.

To relieve the mechanical stresses generated during the preparation stages, all the samples were annealed at ≈160°C for two days in sealed glass tubes, which were first evacuated and then filled with helium.[3)]

[1)] V.P. Shlyakhova took part in this investigation.

[2)] In some experiments, the samples were prepared using quartz and glass capillaries; it was found that the electrical resistance was the same in both cases. Thus, we could assume that molybdenum glass did not contaminate liquid thallium of 99.999% purity during its brief contact with thallium at 400–500°C.

[3)] Separate measurements on samples prepared by the simple filling of capillaries (without rolling) indicated that these samples suffered cold working, which was evidently due to the difference between the linear expansion coefficients of glass and thallium (thallium wets glass

To estimate the influence of possible accidental bending—during the mounting of the very plastic thallium samples—on the electrical resistance, two wires, 2.4 and 2.2 mm in diameter, were bent through ≈90° at eight or nine points. Immediately after this treatment, the resistance was measured at 5—2.5°K and compared with the values obtained before deformation. It was found that such deformation (which was much stronger than that which could be produced by possible accidental bending) increased the relative resistance by ≈25% at 2.5°K, and 5% at 5°K. Bearing this in mind, the annealed samples were mounted on Getinaks (resin-impreganted board) sheets to avoid any mechanical cold working during the mounting or during the cooling to 4.2°K. The thinnest samples (< 0.4 mm in diameter) were mounted particularly carefully and the electrical contacts were provided by copper wire, 0.1—0.05 mm in diameter, twisted into a spiral. In all the cases, the current contacts were soldered to the thallium samples by Wood's alloy and the potential contacts were spark-welded.

The electrical resistance was measured employing the usual compensation circuit of $\approx 4 \times 10^{-8}$ V voltage sensitivity. At room temperature, the measuring current was 30—60 mA; at helium temperatures, it was 1--7 A. This made it possible to measure the resistance at helium temperatures with an accuracy of 5—3% for thick samples and ≤ 1% for thin samples.[4)]

To destroy the superconductivity of thallium in the temperature range 1.6—2.4°K, we used a solenoid with a constant of 52.5 Oe/A, in which a uniform (±1%) field up to 2.5 kOe was established in the middle part of the solenoid.

All the measurements were carried out in the temperature range 1.5—5.1°K in a metal cryostat. Temperatures below 4.2°K were reached in a helium bath by pumping helium vapor; temperatures above 4.2°K were produced by establishing an excess pressure up to ≈1.3 excess atm. The bath temperature was determined from the vapor pressure of helium using the 1958 scale. A constant temperature in the cryostat was maintained with a "monostat" to within 0.002° at temperatures of 2.7—5.1°K, and to within 0.02—0.005° at temperatures of 1.5—2.6°K.

RESULTS AND DISCUSSION

The experimental temperature dependence of the relative electrical resistantance $\delta_T = R_T/R_{295}$ where R_T and R_{295} are the values of the resistance at a given temperature T and at 295°K) of thallium samples of various diameters d are presented in Fig. 1. In order to avoid the overcrowding of this figure, some of the curves obtained are omitted. The main results for all the samples are listed in Table I.

very well). The cold-working stresses were relieved slowly, even at room temperature, as indicated by the fall of the resistance of the same sample during several days. Annealing at 160°C for two days obviously relieved all the mechanical stresses because the resistance of the samples so treated did not vary with time.

[4)]Preliminary measurements at 2°K, carried out on thick wires using a current of 3—7 A, showed that the magnetic field of the current itself did not affect, within the limits of the experimental error, the resistance of thallium.

Table I

d, mm	$10^4\delta_0$	$10^4\delta_3$	$10^4\delta_{4,2}$	$10^4\delta_5$	m	10^7A
0.125	1.83	2.095	2.895	4.04	4.20	2.58
0.168	1.44	1.705	2.55	3.715	4.25	2.44
0.185	1.42	1.690	2.52	3.70	4.20	2.65
0.188	1.405	1.645	2.425	3.525	4.30	2.16
0.265	1.13	1.375	2.11	3.185	4.20	2.38
0.275	1.00	1.240	2.03	3.18	4.30	2.16
0.326	0.91	1.165	1.945	3.11	4.30	2.12
0.340	0.87	1.107	1.82	2.89	4.30	2.0
0.487	0.60	0.860	1.60	2.705	4.25	1.98
0.565	0.612	0.860	1.615	2.73	4.30	2.15
0.685	0.51	0.76	1.52	2.64	4.30	2.10
1.28	0.33	0.57	1.317	2.48	4.60	1.39
2.20	0.32	0.53	1.308	2.47	4.65	1.31
2.41	0.33	0.52	1.273	2.435	4.60	1.30
∞	0.23	0.42	1.15	2.31	4.60	1.30

At $T \leq 2.25$°K, the measurements of the resistance were carried out in the longitudinal field of the solenoid. To correct for the influence of the magnetic field (of the order of the critical field H_c) on the resistance, the dependence of the resistance on the magnetic field was recorded for each sample and extrapolated quadratically to find the resistance in H = 0. Although the increase in the resistance in the external magnetic field was small, it was necessary to make a correction to eliminate its influence on the relative residual resistance δ_0 and on the power exponent m

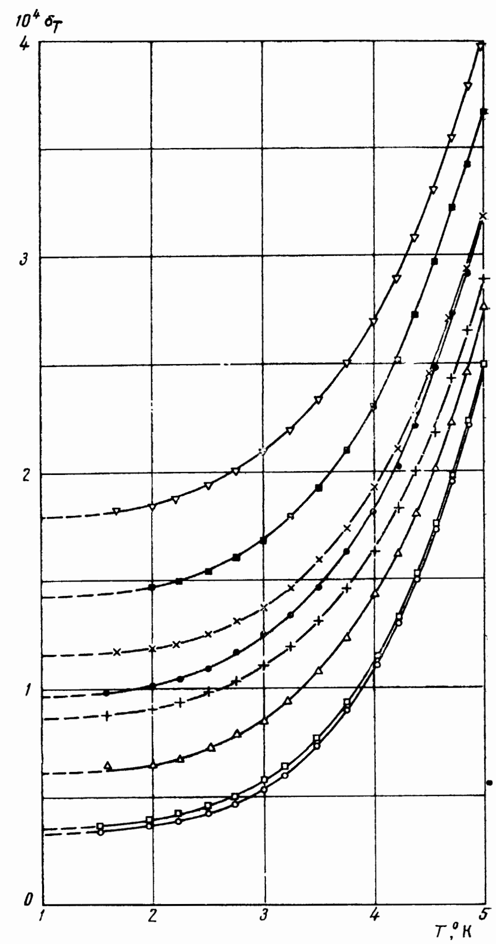

FIG. 1. Temperature dependence of the relative resistance of polycrystalline thallium samples of different diameters: ○ – d = 2.41; □ – d = 1.29; Δ – d = 0.565; + – d = 0.34; ● – d = 0.275; X – d = 0.265; ■ – d = 0.185; ∇ – d = 0.125 (d in mm).

of T. This increase in the resistance was greatest (≈12%) for the thickest sample (d = 2.4 mm) and smallest (< 1%) for the thinnest sample (d = 0.125 mm). Figure 1 shows the experimental points (at T < 2.4°K) obtained after the extrapolation of the corresponding resistance to zero magnetic field.

It is clearly evident from the curves in Fig. 1 that the thinner the sample the higher is the position of the whole curve. The influence of the wire diameter on the temperature dependence of the resistance of thallium could be deduced from the graphs representing $\delta_T = f(T)$ for all the samples.

To determine this influence, the temperature dependences of the resistance of all the samples were described by fitting an empirical equation $\delta_T = \delta_0 + AT^m$ to each experimental curve by a suitable selection of the constants δ_0, A, and m, which gave the best agreement between the calculated and experimental points. To determine these constants, we selected two points which were furthest apart on the temperature scale: at 2 and 5°K. The error in the determination of m by such a method was ±0.05 for the thinnest samples and ±0.1 for the thickest ones. The well-known theoretical equation $\delta_T = \delta_0 + \alpha T^2 + \beta T^5$ was not obeyed by any of the samples below 3°K and the deviations from it were so large that it could not be used. Good agreement with the experimental curves was obtained using the equation $\delta_T = \delta_0 + B_1T^4 + B_2T^5$, but there is as yet no physical interpretation of this equation and, therefore, we shall not discuss it further.

Results of an analysis of all the curves using the empirical equation are given in Table I, which shows a definite tendency for m to decrease and for A to increase when the thickness of the samples is reduced. No monotonic decrease of m can be deduced because of a large error in its determination. The dependence of m on the diameter d is in qualitative agreement with the results of theoretical papers,[6,7] although quantitative comparisons cannot be made: no convenient calculation formulas are available. From the results presented in Table I, it follows that the influence of the size on the value of m is not very strong: when the diameter is reduced by a factor of 20, m changes by only 10%, although the mean free path λ_0 at 0°K is 8 times greater than the diameter of the thinnest wire.

Table II

T, °K	$10^4\delta_T$	T, °K	$10^4\delta_T$	T, °K	$10^4\delta_T$
0	0.332	2.75	0.465	4.21	1.290
1.53	0.340	3.00	0.530	4.45	1.570
1.75	0.348	3.25	0.620	4.60	1.785
1.97	0.364	3.50	0.740	4.75	2.020
2.23	0.385	3.75	0.893	5.00	2.460
2.50	0.420	4.00	1.080	5.12	2.70

The electrical resistance of the thickest sample, which is typical of thallium of a given purity, is presented separately in Fig. 2 and Table II. The continuous line in Fig. 2, drawn through the experimental points, represents an equation $\delta(T) = 1.33 \times 10^{-7} T^{4.6}$, while the dashed line represents a dependence $\delta(T) \propto T^5$. The empirical value obtained m = 4.6, is halfway between the corresponding values of m reported in [3,4]. Evidently, this value is governed by the purity of the metal because the purer the metal the closer is the value of m to 5, as observed for Al, Cd, In, and Sn.[8] In fact, judging by the resistance, our thallium was 17 times purer than the metal used in [3], for which m = 4, and half as pure as the metal used in [4], for which m = 5.

The graphs in Fig. 1 were used to plot the dependences $\delta_T = f(1/d)$ at temperatures of 5, 4.2, 3, and 0°K, given in Fig. 3. The horizontal segments in Fig. 3 represent the error in the measurement of the diameter. The error in the measurement of the resistance was within the limits of the error of plotting the experimental points, even for the thickest samples. It follows from Fig. 3 that at all temperatures the experimental points fit well a family of straight lines with

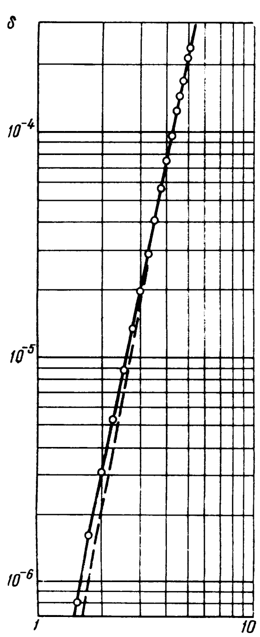

FIG. 2. Temperature dependence of the ideal relative resistance of bulk (d = 2.41 mm) thallium.

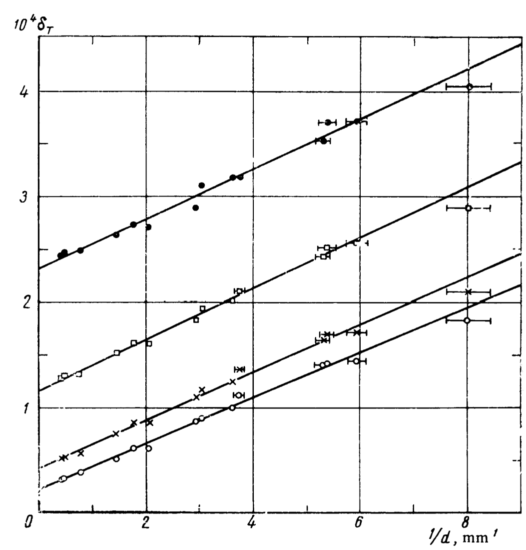

FIG. 3. Effect of size on the relative resistance of thallium at four temperatures (in °K): ● – 5; □ – 4.2; X – 3; ○ – 0.

almost the same slope.[5] We find that:

T, °K:	0	3	4.2	5
$10^6 \tan\varphi$, cm	2.18	2.28	2.44	2.54

Nevertheless, the slope of the straight line for 0°K is least: it is equal to $\tan\varphi = 2.18 \times 10^{-6}$ cm and increases monotonically with temperature to become ≈ 18% larger at 5°K than at 0°K. We may expect the slope to increase considerably when the temperature is increased further, as in the case of Al.[9] The temperature dependence of $\tan\varphi$ indicates that the electron-phonon interaction affects the size effect, which increases when the sample diameter is reduced and the test temperature increased.[6,7]

The mean free path of electrons was estimated from the formula [9]

$$\delta_{d,T} = \delta_{\infty,T}(1 + \lambda / d)$$

(the subscript ∞ refers to bulk samples) and the reflection of electrons from the surface of a sample was assumed to be completely diffuse. If the reflection from the surface were not wholly diffuse, the value of λ would be larger. Unfortunately, there is as yet no agreed view about the nature of the reflection of electrons from the surface of a metal although there have been several investigations [10] in which it is concluded that the reflection is partly diffuse and partly specular. The value of δ_∞ at each temperature was determined by the extrapolation of the straight lines in Fig. 3 to the value $1/d = 0$. The following values of λ at various temperatures were obtained from $\tan\varphi = (\delta_0\lambda)_\infty$ and $\delta_{\infty,T}$:

T, °K:	0	3	4.2	5
λ, мм:	1.0	0.5	0.2	0.1

Our results for λ_0 are compared in Table 3 with those obtained by other authors: they show good agreement with two investigations reported in [11,12].

Using the results of the extrapolation of the resistance to infinite diameter, we determined the change in the resistance of thallium corresponding to a reduction in the temperature from 4.2 to 0°K, which was found to be $(\delta_{4.2}/\delta_0)_\infty = 4.8$.

From the tabulated value $\rho_{295} = 19.7 \times 10^{-6}\ \Omega\cdot$cm, we calculated the product $(\rho\lambda)_\infty = 4.3 \times 10^{-11}\ \Omega\cdot\text{cm}^2$, which was in good agreement with $\rho\lambda = 4 \times 10^{-11}\ \Omega\cdot\text{cm}^2$ obtained by Zavaritskiĭ.[4] Knowing $(\rho\lambda)_\infty$, we could calculate the conduction electron density per unit volume in thallium using the formula

$$(\rho\lambda)_\infty^{-1} = \left(\frac{8\pi}{3}\right)^{1/3} \frac{e^2}{h} n^{2/3} = 7.9\cdot 10^{-5} n^{2/3} [\ \Omega\cdot\text{cm}^2\ ].$$

This value was found to be $n = 5.4 \times 10^{21}$. Next, having calculated the number of atoms per unit volume $n_a = 3.5 \times 10^{22}$, we found the ratio of conduction electrons per atom: $n/n_a = 0.15$. This value of n/n_a was much less than 3, predicted by the classical theory.

[5]The small scatter of the experimental points indicated satisfactory averaging of the electrical properties of anisotropic (at T < 230°C) thallium in the method selected for the preparation of samples, since the size effect of such metals should have a considerable anisotropy (the slope of the lines should depend on the crystallographic orientation), of the type observed first for Sn and Zn.[9]

Table III

Nature of Investigation	$10^5\delta_0$	λ_0, mm	Reference
Absorption of ultrasound in magnetic field	1.0	1.5	[11]
	100	$6.7\cdot 10^{-4}$	[12]
Effect of size on resistance	1.2	1.7	[4]
	2.3	1.0	Present study

It is worth noting that the scattering of electrons on grain boundaries should not have affected the size effect, since the grain size was, as a rule, comparable with or larger than the wire diameter. Consequently, the wires actually consisted of separate single-crystal regions, and in the majority of cases an electron traveling toward the surface did not meet any grain boundaries.

Bearing in mind that λ and d were comparable at helium temperatures, we attempted to detect the size effect in a longitudinal magnetic field, in the same manner as has been done in investigations of Sn, Zn, Al, and In.[13] Our measurements showed that the effect did exist, but to obtain unambiguous results such an investigation should be carried out on single crystals of one orientation.

It should also be mentioned that the observed increase in the resistance due to repeated bending of a sample varied linearly with temperature in the range 5–2.5°K, in agreement with Matthiessen's rule.

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